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SUMMARY

As part of a continuing effort to develop thermal barrier systems for advanced aircraft gas turbine engine components, systems consisting of Ni-base bond coatings containing about 16Cr, 6Al, and from 0.15 to 1.08Y (all in wt. %) and zirconium oxide layers containing from 4.0 to $24.4Y_2O_3$ (in wt. %) were evaluated. The evaluations were done in a cyclic furnace between 990° - 280° C and 1095° - 280° C on solid specimens; in a natural gas-oxygen torch rig between about 1200° - 100° C on solid specimens and up to 1580° C surface temperatures on air-cooled blades; and in a Mach 1.0 burner rig up to 1570° C surface temperatures on air-cooled blades.

The data indicate that the best thermal barrier systems consisted of combinations involving the Ni-16.4Cr-5.1Al-0.15Y and Ni-17.0Cr-5.4Al-0.35Y bond coatings and the $6.2Y_2O_3$- and $7.9Y_2O_3$- (all in wt. %) stabilized zirconium oxide layers. In furnace cyclic tests these thermal barrier systems withstood 1500 1-hour cycles between 990° - 280° C and over 100 1-hour cycles between 1095° - 280° C. In a natural gas-oxygen torch rig these systems on solid specimens withstood approximately 590 to 790 1-hour cycles between 1200° - 100° C. On air-cooled

blades the NiCrAl-0.15Y/ZrO $-6.2Y_2O_3$ (in wt. %) at 1580° C surface temperature and the NiCrAl-0.35Y/ZrO $-7.9Y_2O_3$ (in wt. %) at 1550° C surface temperature withstood over 1300 and 1500 1-hour cycles without failure, respectively. In the Mach 1.0 burner rig the above two systems withstood over 1400 and 2000 1-hour cycles without failure at about 1480° and 1470° C surface temperatures, respectively.

All failures seem to be initiated through the formation of parallel crack or cracks within the zirconium oxide layer near the bond coating-zirconium oxide layer interface. The external cracks within the oxide layers on solid specimens were at 90° angles to the bond coating while those on air-cooled blades were either at 90° or at 35° - 45° angles to the bond coating.

INTRODUCTION

Thermal barrier systems have been under development for many years. Attempts have been made to use such systems in regeneratively cooled rocket engines (refs. 1 to 3), on aircraft gas turbine components (refs. 4 and 5), and on air-cooled turbine blades and vanes (ref. 6). However, all of these attempts ended with very little overall success at high temperatures. Furthermore, Nijpjes (ref. 7) evaluated various bond and thermal barrier coatings and found that Nimonic 115 alloy was a better bond coating than nichrome for calcia-stabilized zirconia. However, he reported that adherence was still a major problem at high temperatures.

Most recently, this author developed a new approach for improving the adherence of thermal barrier systems (refs. 8 to 10). The data in references 8 and 9 showed that Ni-16.2Cr-5.6Al-0.61Y (in wt. %) bond coating with a ZrO_2-11.6Y_2O_3 (in wt. %) layer are better than nichrome and calcia-stabilized zirconia. The Ni-16.2Cr-5.6Al-0.61Y/ZrO_2-11.6Y_2O_3 system on flat specimens withstood hundreds of 1-hour cycles between 975° and 280° C without cracking or spalling. This NiCrAl-0.61Y/ZrO_2-11.6Y_2O_3 system on air-cooled blades withstood over 200 1-hour cycles in Mach 0.3 burner rig tests at surface temperatures up to 1490° C without cracking or spalling. Furthermore, this system also successfully withstood 500 short cycles in a J-75 engine (ref. 11) and 845 1-hour cycles in a Mach 1.0 burner rig at about 1290° C surface temperature (ref. 9).

To further improve the NiCrAlY/ZrO_2-Y_2O_3 system for aerospace application, this study was conducted to examine the effects of yttrium concentration in the bond coating and yttria concentration in the zirconium oxide layer on the thermal barrier system adherence and performance. These effects on the adherence and performance were studied by cyclic furnace, cyclic natural gas-oxygen torch burner rig, and cyclic Mach 1.0 burner rig tests.

MATERIALS, APPARATUS, AND PROCEDURE

Materials

The compositions of plasma spray powders of Ni-Cr-Al-Y (-200 to +325 mesh) and yttria-stabilized zirconia (-200 to +325 mesh) are presented in table I. The substrates were nickel-base alloys - B-1900 with hafnium (Hf) and conventionally cast MAR-M-200 with Hf. The cobalt alloy MAR-M-509 was also used. The compositions of these alloys are also presented in table I. The bond and oxide coating compositions throughout this report are expressed in weight percent.

Flat specimens, 2.5x1.3x0.25 cm, with all corners and edges rounded to about 0.16 cm radius were used in cyclic furnace tests and 7.5x1.3x0.5 cm specimens rounded to about 0.25 cm radius were used in cyclic natural gas-oxygen torch burner rig tests. Cast B-1900 with no hafnium but otherwise the same as B-1900 with hafnium (table I) air-cooled turbine blades for a J-75 engine were used in cyclic natural gas-oxygen and cyclic Mach 1.0 burner rig tests. These blades, that were previously aluminized and exposed in engine operation for 200 to 500 hours, were stripped of the aluminide coating before applying the thermal barrier coating system.

Apparatus and Procedure

Plasma spray coating deposition. - All sample surfaces were grit blast cleaned with alumina and within 10 minutes the NiCrAlY bond coating was applied with a plasma spray gun (350 amperes and 27 volts) to a thickness between 0.005 and 0.015 cm. The ZrO_2-Y_2O_3 coatings were also applied by a plasma spray gun (550 amperes and 32 volts) within 20 minutes of completing the NiCrAlY bond coating. Zirconium oxide coatings on flat specimens were about 0.038 cm thick while those on air-cooled blades were nominally 0.038, 0.055, or 0.065 cm thick. Actual coating thicknesses are specified in the figures.

Plasma spraying of both coatings was done in an open air environment using argon as the plasma gas. The plasma spray gun-to-substrate distance was maintained at about 13 to 15 cms.

In the furnace cyclic tests coated specimens were heated in air to either 990° or 1095° C. The cycle in both cases consisted of 6 minutes heat-up, 60 minutes at temperature, and 60 minutes cooling to about 280° C. Specimens from the 990° and 1095° C tests were removed and inspected for cracks at least every 12 cycles until visible external cracks appeared in the oxide coatings. The specimens were removed from the furnace for inspection at temperatures between 350° and 400° C. Because of this arrangement, the flat coated specimens that withstood 1500 1-hour cycles at 990° C were cooled to room temperature at least 125 times. The temperature in the furnace was measured with a platinum - platinum-13 percent rhodium thermocouple.

Both flat coated specimens and air-cooled J-75 blades were tested in the natural gas-oxygen torch burner rig. The blades were air-cooled at about 14 - 17 gms/second airflow. Both, flat and air-cooled specimens were held in a fixed position. For flat specimens only, two torches were used and for air-cooled blades four torches were used as shown in figure 1.

The cyclic tests in the Mach 1.0 burner rig were conducted on air-cooled blades only. The blade was held in a fixed position as is shown in figure 2. The area of the hot zone was about 6.5 cm^2 along the leading edge. A larger area on the pressure side near the trailing edge was also heated. The true surface temperatures of the coated blades and coated flat specimens in natural gas-oxygen and Mach 1.0 burner rigs were established by means of calibration curves obtained by comparing the thermocouple bulk and surface optical pyrometer temperatures of the flat coated uncooled specimens as described in reference 8. The temperature measurement is estimated to be accurate to about ±2 percent at 1320° C. The substrate temperatures at the bond coating-substrate interface in the coated air-cooled blades were measured with embedded Chromel-Alumel thermocouples.

RESULTS AND DISCUSSION

Cyclic Furnace Testing

The adherence and performance of several yttria-stabilized zirconia coatings containing between $4.0Y_2O_3$ and $24.4Y_2O_3$ on Ni-base bond coatings containing about 16Cr, 6Al, and between 0.15Y and 1.08Y (all compositions are in wt. %) were studied at 990° and 1095° C in cyclic furnace tests. B-1900 with hafnium and in some cases MAR-M-509 coupons coated with these systems were used in all furnace studies.

The above yttria concentrations in zirconia were chosen because it has been reported that about $12Y_2O_3$ is required to achieve total stabilization of monoclinic zirconia in a cubic phase (ref. 12). It was desired to evaluate the effects of yttria concentrations in zirconia above and below this level. The data obtained in these cyclic furnace studies between 990° and 280° C are presented in table II and show that the performances of thermal barrier systems are very dependent upon the combined compositions of the oxide coatings and the bond coatings. These data suggest that the life of the thermal barrier system decreases as the concentration of yttria in zirconia increases from $6.2Y_2O_3$ to $24.4Y_2O_3$. Decrease of yttria from $6.2Y_2O_3$ to $4.0Y_2O_3$ in zirconia also causes a reduction in life. The data further suggest that at any one yttria level the life of the thermal barrier system decreases as the yttrium concentration in the bond coating increases. The $4.0Y_2O_3$-stabilized zirconia coating seems to be an exception to this trend since its life with the 0.15Y bond coating is shorter than that with the 0.35Y bond coating. The data also show that $6.2Y_2O_3$-stabilized zirconia coating on Ni-Cr-Al-Y bond coatings containing between 0.15Y and 1.08Y withstood 1500 1-hour cycles without failure. This suggests that the best oxide coating for resisting cyclic oxidation environments might be the yttria-stabilized zirconia containing about $6Y_2O_3$.

The oxide coating and the bond coating compositions reported in table II were also evaluated at 1095° C and the results are presented in table III. Comparing the data in tables II and III it becomes apparent that again the best zirconium oxide coating contains $6.2Y_2O_3$ and the best bond coating is Ni-16.4Cr-5.1Al-0.15Y. It is also apparent that the lives of thermal barrier systems are very sensitive to temperature. Specimens coated with NiCrAl-0.15Y/ZrO_2-$6.2Y_2O_3$ did not fail at 990° C after 1500 1-hour cycles but at 1095° C they failed after only 112 1-hour cycles. The data in table III for the $4.0Y_2O_3$-stabilized zirconia coating seem to be in agreement with those in table II.

To gain some understanding as to what could be happening, X-ray diffraction analyses were performed on the various oxide coatings before and after testing. The data in table IV show, as expected, that by increasing the nominal yttria concentration in spray powder from $11.5Y_2O_3$ to $24.4Y_2O_3$ the amount of monoclinic zirconia phase decreases before and after testing. At the $17.4Y_2O_3$ and $24.4Y_2O_3$ concentrations, excess Y_2O_3 was observed both before and after testing. By reducing the concentration of yttria in zirconia to $6.2Y_2O_3$ and $4.0Y_2O_3$ the amount of monoclinic zirconia phase present before and after testing increased as expected. Thus, the data in tables II, III, and IV indicate that to achieve long life in cyclic oxidizing environment tests the oxide coating must contain some monoclinic zirconia. Furthermore, the presence of excess yttria in zirconia seems to adversely affect the life of the thermal barrier system.

To obtain a better understanding of the effect of yttria in the zirconium oxide coating and the yttrium in the bond coating, specimens were subjected to metallographic examination. The comparison of the microstructures before and after testing seems to indicate that the microstructure of the oxide coating has changed very little even after 1498 1-hour cycles at 990° C as can be seen by comparing figures 3(a) and (b). The oxide coating in figure 3(a) was thinner than those actually tested. There seems to be very little change in the porosity of the oxide coating. Close examination of the bond coating after 1498 1-hour cycles at 990° C indicated that it was partially oxidized as can be seen in figure 3(b). Examination of the microstructures of specimens exposed to at least 100 1-hour cycles at 1095° C showed that the oxide coating microstructures were not significantly different from those exposed at 990° C after 1498 1-hour cycles. However, it was observed that the bond coating from the 1095° C cyclic test was more oxidized than the bond coating from the 990° C test after 1498 1-hour cycles. Furthermore, examination of bond coatings containing various concentrations of yttrium suggests that as the yttrium content increases, the oxidation of the entire bond coating seems to decrease. However, it should be remembered that the thermal barrier systems whose bond coatings contain 1.08Y fail significantly faster than those containing only 0.15Y.

Furthermore, it was found from the optical metallographic examination of microstructures of many specimens, exposed at 990° and 1095° C, that the failures always occurred within the oxide coating but very near the bond coating-oxide coating interface. Failure occurs due to formation of a small crack parallel to the bond coating as shown in figure 4. The presence of such very small cracks was even observed in specimens that did not as yet have a visible external crack. Therefore, it may be deduced that the cracking of the oxide coating is initiated from within the oxide coating near the bond coating-oxide coating interface. The likelihood that cracking will initiate within the oxide coating near the bond coating-oxide coating interface is also suggested by the data reported by Levine (ref. 13). He studied the adhesive/cohesive strength of a $NiCrAlY/ZrO_2$-$12Y_3O$ thermal barrier system and found that the failures occurred within the oxide coating near the bond coating-oxide coating interface.

From the photomicrographs in figures 3 and 4 it is apparent that the substrates have a diffusion zone near the substrate-bond coating interface. In the B-1900 with Hf (fig. 3(b)) it is believed that the substrate was depleted of aluminum or the γ' phase. This is very similar to the behavior encountered by Barrett and Lowell (ref. 14). The diffusion zone in MAR-M-509 has no aluminum and therefore this zone could be formed through the diffusion of tungsten, chromium, carbon, and/or nickel in the bond coating. Further evaluation must be made to determine exactly what elements are being depleted. The effect of this element diffusion and the presence of the diffusion zone on the life of the thermal barrier system still remains to be evaluated.

Cyclic Natural Gas-Oxygen Torch Burner Rig Testing of Flat Specimens

To expose flat coated specimens to greater thermal shocks than those possible in the furnace tests, the two-layered thermal barrier systems were also tested in natural gas-oxygen torch burner rigs similar to the torch burner rig in figure 1. In such rigs which use two torches to heat the specimen from two sides the desired temperature was normally reached in less than 3 minutes, the specimen was exposed for 60 minutes at temperature, and cooled to about 100° C in less than 5 minutes. The test data are presented in table V. The data again show that as the yttrium concentration in the bond coating and yttria concentration in the oxide coating increase, the life of the thermal barrier system decreases. However, again the 4.0Y_2O_3-stabilized zirconium oxide coating failed faster than the 6.2Y_2O_3-stabilized zirconia coating. These data are in complete agreement with the data reported in tables II and III. The data again show that in the torch burner rig tests the best thermal barrier system is the Ni-16.4Cr-5.1Al-0.15Y/ZrO_2-6.2Y_2O_3 system which is about twice as good at the Ni-17.0Cr-5.4Al-0.35Y/7.9Y O and Ni-16.4Cr-5.1Al-0.15Y/ZrO_2-4.0Y_2O_3 thermal barrier systems. The data in table V show that the best thermal barrier system mentioned above withstood over 790 1-hour cycles under these severe thermal conditions.

All of the various thermal barrier systems studied in the natural gas-oxygen torch burner rig failed in the same manner - cracking within the oxide coating near the bond coating-oxide coating interface - as those in the cyclic furance tests except for the 4.0Y_2O_3-stabilized zirconia coating. Cracks at about the middle of the oxide coatings were also observed (fig. 5) and although such cracks sometimes did not surface they did continue inward to the parallel crack within the oxide coating near the bond coating-oxide coating interface. The 4.0Y_2O_3-stabilized zirconia coating failed not only by formation of a crack but in addition was observed to become powdery along the edge of the hot zone.

Cyclic Natural Gas-Oxygen Torch Burner Rig Testing of Air-Cooled Blades

To expose the thermal barrier systems not only to even greater thermal shock but also to greater temperature gradients through and along the surface of the oxide coating, air-cooled coated J-75 engine blades were tested in the natural gas-oxygen torch burner rig shown in figure 1. Three kinds of bond coatings and three kinds of oxide coatings were evaluated. The test data are presented in figure 6. These data again suggest that life increases when yttria concentration in the zirconium oxide coating and the yttrium concentration in the bond coating decrease. This is apparent from the data represented by the first, third, and fourth bars in figure 6. This trend under more severe conditions is in agreements with the trend observed in the cyclic furnace tests. It is also apparent from the data in figure 6 that the thickness of the thermal barrier coating is very important. As the thickness of the thermal barrier coating increases the substrate temperature decreases, as shown by the data represented by the first two bars in figure 6. Decreasing the substrate temperature from 950° to 895° C increased the life of the thermal barrier coating from 480 to 1120 1-hour cycles. It is believed that the yttrium diffusion in the bond coating toward the thermal barrier coating and the rates of oxidation and degradation of the bond coating are smaller at the lower temperature. Furthermore, the stresses within the oxide coating at or near the oxide coating-bond coating interface at lower temperature are smaller than those at the higher temperature.

The oxide coating failures on the air-cooled J-75 blades were very similar to those encountered with the uncooled coated flat specimens in the cyclic furnace and natural gas-oxygen torch burner rig tests. Such failures occurred within the hot zone with the appearance of one or more cracks. Oxide coatings on J-75 blades failed in one of two ways as is shown in figure 7. A hairline crack would occur on the leading edge as shown in figure 7(a). Normally, this crack is just about perpendicular to the crack or cracks within the oxide thermal barrier coating near the bond coating-thermal barrier coating interface. The second type of failure observed in coated J-75 blades was the formation of a crack between a 35° to 45° angle to the bond coating-oxide coating interface as shown in figure 7(b). This acute angle crack normally formed toward the suction side of the blade. Very few blades had both types of cracks present. In almost all cases neither type of a crack penetrated all the way through the thermal barrier coating to the bond coating. However, it was observed that such parallel cracks that formed within the oxide coating near the bond coating-oxide coating interface, as illustrated in figure 7, seemed to touch this interface as shown in figure 7(a).

The ZrO_2-4.0Y_2O_3 coating on J-75 blades became powdery along the edge of the hot zone. Powdering usually occurred after about 150 1-hour cycles at about 1550° C surface temperature. Around the hot zone the powder eroded and the oxide coating-free area increased in width until at the end of 200 1-hour cycles it was about 1 cm wide in some places. After 200 1-hour cycles this oxide coating also developed a small crack within the hot zone. It is believed that this behavior is due to the stresses along the edges of the hot zone and because the 4.0Y_2O_3-stabilized zirconia thermal barrier coating is closer in its properties to pure zirconia. Pure zirconia bodies will turn into powder after being cycled repeatedly through the monoclinic-tetragonal phase transformation temperature.

Cyclic Mach 1.0 Burner Rig Life Testing

Thermal barrier systems are projected for use in jet engines at very high temperatures. For this reason it was decided to also evaluate the thermal barrier systems in a Mach 1.0 burner rig where the test conditions are closer to the thermal conditions encountered in jet engines than in other testing equipment previously described. Of particular interest were the high gas velocity and the more rapid thermal transient effects.

All surface temperatures up to 1570° C were reached within 30 seconds and specimens cooled to less than 75° C substrate temperature within 20 seconds. Cyclic testing in the Mach 1.0 burner rig was done on three thermal barrier systems. The data in figure 8 show that in Mach 1.0 burner rig tests the oxide coatings withstood severe temperature gradients (up to 600° C through the oxide coatings) for hundreds of 1-hour cycles before a crack appeared in the hot zone. Furthermore, there are large temperature gradients along the surface of the thermal barrier coated blade as can be seen by the colors of the blade exposed to the stream of the hot gas in figure 2. However, in spite of these very large temperature gradients through the coating and along the surface of the coating, all of the coated blades withstood hundreds of 1-hour cycles.

The data in figure 8 represented by the first and second bars again confirm that the yttrium concentration in the bond coating and yttria concentration in the zirconium oxide coating have very significant effects on the life of the thermal barrier system. Decreasing yttrium concentration from 0.61Y to 0.35Y and lowering the yttria concentration in the zirconium oxide coating from 11.5Y_2O_3 to 7.9Y_2O_3 resulted in an increase in life from about 850 to 2000 1-hour cycles. Even after 2000 1-hour cycles no failure was observed for the Ni-17.0Cr-5.4Al-0.35Y/ZrO -7.9Y_2O_3 thermal barrier system. The data in figure 8 represented by the third bar show that the Ni-16.4Cr-5.1Al-0.15Y/ZrO_2-7.9Y_2O_3 thermal barrier system withstood over 1400 1-hour cycles without failure and, therefore, in this type of test this thermal barrier system is also better than the originally developed NiCrAl-0.61Y/ZrO_2-11.5Y_2O_3 thermal barrier system. Comparison of the data represented by the second, fourth, and fifth bars in figure 8 clearly shows that as the surface temperature increases and generally the substrate temperature increases, also, the life of the thermal barrier system decreases rapidly. The fourth bar shows shorter life at a high surface temperature but at slightly cooler substrate temperature. This thermal barrier system (fig. 8, bar 4) may have failed prematurely or the substrate temperature may not have been as low as indicated.

The data previously reported in references 8 and 9 showed that in Mach 0.3 burner rig tests conducted at high fuel to air ratio to achieve high temperatures, the gas stream contained significant quantities of carbon. Here, the zirconium oxide coating experienced rapid reduction in oxide coating thickness, up to 50 percent of original thickness within some 246 1-hour cycles at 1410° C surface temperature. In all the tests performed in the natural gas-fired Mach 1.0 burner rig no significant reduction in oxide coating thickness was observed. In fact some increase in the thermal barrier coating thickness was noticed. In the latter case it was found that the oxide coatings were covered by about 0.005 cm of iron oxides, and when this occurred some particles from the oxide coating surface broke away upon thermal cycling. Therefore, it is likely that iron oxides react with the zirconium oxide coating and thus contribute to this localized spalling. For this reason such reactions could become a major coating problem in gas streams highly contaminated with iron oxides. Furthermore, since in the Mach 1.0 burner rig tests no significant reduction in oxide coating thickness was observed, the life of the originally developed NiCrAl-0.61Y/ZrO_2-11.5Y_2O_3 thermal barrier system increased from about 246 1-hour cycles in the Mach 0.3 burner rig (refs. 8 and 9) to about 850 1-hour cycles in the Mach 1.0 burner rig before a small crack occurred within the hot zone (fig. 8, bar 1). The failure mechanisms in these two environments were different.

The failures in the thermal barrier systems on air-cooled J-75 blades in the Mach 1.0 burner rig occurred in a manner similar to those in the natural gas-oxygen torch burner rig. Parallel cracks occurred within the oxide coating near the bond coating-oxide coating interface. The first crack on the surface was either perpendicular to or at 35° to 45° angle to this parallel crack. These cracks were similar to those shown in figures 7(a) and (b).

SUMMARY OF RESULTS

Thermal barrier systems of various compositions were studied in cyclic furnace tests between 990° and 280° C and between 1095° and 280° C;

in cyclic natural gas-oxygen torch burner rig tests between 1200° and 100° C on flat uncooled specimens and up to 1550° C surface temperature on air-cooled specimens; and in cyclic Mach 1.0 burner rig tests up to 1570° C surface temperature on air-cooled specimens. The Ni-Cr-Al-Y bond coating was nominally Ni-16Cr-6Al with yttrium concentrations between 0.15 and 1.08. The zirconium oxide coatings contained between 4.0 and 24.4Y_2O_3 (all concentrations are in wt. %). The results from this study showed that:

1. The best life in the 990° C furnace tests was obtained with Ni-16.4Cr-5.1Al-0.15Y bond-coating with 6.2Y_2O_3-, or 7.9Y_2O_3-stabilized zirconia coatings. Both of these systems withstood 1500 1-hour cycles without cracking or spalling. In the 1095° C furnace tests the best coating system was Ni-16.4Cr-5.1Al-0.15Y/ZrO -6.2Y_2O_3 which withstood 112 1-hour cycles. In contrast, the 24.4Y_2O_3-stabilized zirconia coating with the same bond coating withstood only 535 1-hour cycles to 990° C and only about 42 1-hour cycles to 1095° C.

In the natural gas-oxygen torch burner rig tests the best thermal barrier system was again Ni-16.4Cr-5.1Al-0.15Y/ZrO_2-6.2Y_2O_3 followed closely by Ni-17.0Cr-5.4Al-0.35Y/ZrO_2-6.2Y_2O_3, and Ni-16.4Cr-5.1Al-0.15Y/ZrO_2-7.9Y_2O_3 which withstood over 790, 620, and 580 1-hour cycles to 1200° C, respectively. In comparison a thermal barrier system, NiCrAl-0.61Y/ZrO_2-11.5Y_2O_3, closely approximating the best original system, withstood only 157 1-hour cycles to 1200° C. On air-cooled blades, the Ni-17.0Cr-5.4Al-0.35Y/ZrO_2-7.9Y_2O_3 and Ni-16.4Cr-5.1Al-0.15Y/ZrO_2-6.2Y_2O_3 thermal barrier systems at 1550° C surface temperature withstood some

1500 and 1300 1-hour cycles, respectively. No failure was observed. Again, the originally developed NiCrAl-0.61Y/ZrO -11.5Y_2O_3 thermal barrier system failed after 1120 1-hour cycles at 1390° C surface temperature.

In the Mach 1.0 rig tests the NiCrAl-0.35Y and NiCrAl-0.15Y bond coatings with a ZrO_2-7.9Y_2O_3 coating withstood over 2000 1-hour cycles at a 1470° C surface temperature and over 1400 1-hour cycles at a 1480° C surface temperature without failure, respectively.

2. The data show that in order to obtain long thermal barrier system life the yttria concentration in the zirconium oxide coating should be between 6 and 8w/o. Whenever no monoclinic zirconia phase is present and/or free yttria is present in yttria stabilized zirconia containing 12Y_2O_3 or more, then the oxide coating will fail very rapidly. The data also show that the performance of the thermal barrier system is very sensitive to the concentration of yttrium in the bond coating. Those bond coatings that contained about 1.08Y failed rapidly as compared to those that contained 0.15Y or 0.35Y. The best bond coating compositions were Ni-16.4Cr-5.1Al-0.15Y and Ni-17.0Cr-5.4Al-0.35Y.

3. The lives of thermal barrier systems are very sensitive to substrate temperature. It seems that as the substrate temperature increases the life of the thermal barrier system decreases.

4. The data from the natural gas-oxygen torch burner rig and the Mach 1.0 burner rig tests show that the NiCrAl-0.15Y/ZrO_2-7.9Y_2O_3, NiCrAl-0.15Y/ZrO_2-6.2Y_2O_3, and NiCrAl-0.35Y/ZrO_2-7.9Y_2O_3 thermal barrier

systems can withstand very large temperature gradients along the surface and through the oxide coatings (up to 600° C). These large temperature gradients did not cause cracking or spalling over hundreds of 1-hour cycles.

5. All thermal barrier system failures appear to have originated with the formation of a crack or cracks within the oxide coating near the bond coating-oxide coating interface. The externally visible cracks in the oxide coatings on the air-cooled coated blades traversed the oxide coating at 90° or between 35° and 45° angles to the cracks parallel to and near the bond coating-oxide coating interface.

6. No appreciable reduction in oxide coating thickness was observed in the Mach 1.0 burner rig tests. The localized surface spalling that did occur was observed to occur when iron oxide was deposited on the surface of the oxide coating. It is believed that iron oxide reacts with zirconium oxide and causes small particles to spall from the surface.

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13. S. R. Levine, "Adhesive/Cohesive Strength of a ZrO_2-1-2w/o Y_2O_3/ NiCrAlY Thermal Barrier Coating," NASA TM-73792, 1978.

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TABLE I - TYPICAL COMPOSITIONS OF SPRAY POWDERS AND SUPERALLOY SUBSTRATES.

Element	Composition, wt %				
	Bond coating	Thermal barrier oxides		Nickel-base substrate	Cobalt-base substrate
	NiCrAlY[a]	ZrO_2-Y_2O_3 (Standard)	ZrO_2-Y_2O_3 (Nuclear)	B-1900 + Hf	MAR-M-509
Al	[a]4.9 - 5.5	0.009	0.009	6.17	[b]ND
B	<.001	<.001	<.001	<.003	<0.001
C	.007	ND	ND	.008	.63
Ca	ND	.055	.031	<.001	.001
Co	.034	<.005	<.005	10.43	Major
Cr	[a]16.3 - 17.0	ND	ND	8.24	23.64
Cu	.014	ND	ND	<.002	<.001
Fe	.041	.038	.047	.06	.58
Hf	<.01	1.60	.022	1.22	.01
K	<.001	<.001	<.001	<.001	.001
Li	<.001	<.001	<.001	<.001	.001
Mg	<.001	.030	.036	<.001	.001
Mn	.011	<.001	<.001	<.001	<.01
Mo	<.005	<.005	<.005	5.79	.005
Na	<.001	<.001	<.001	<.001	.001
Nb	.039	.005	.005	<.005	.005
Ni	Major	.027	.005	Major	10.62
O_2	.022	ND	ND	ND	ND
P	.01	ND	ND	ND	ND
Pb	ND	ND	ND	<.005	.005
S	.01	ND	ND	<.01	<.01
Si	.082	.057	.044	<.01	.22
Sr	.01	.01	.01	ND	ND
Ta	<.05	.02	.02	4.13	3.77
Ti	.012	.045	.015	ND	.16
V	.031	<.001	<.001	<.001	.69
W	<.01	<.005	<.005	.01	6.96
Y	[a]0.13 - 1.1	[c]3 - 20	[c]6 - 20	ND	ND
Zn	<.05	<.05	<.05	<.05	<.05
Zr	ND	Major	Major	.07	.53

[a]Aluminum, chromium, and yttrium concentrations for various bond coatings used are given in tables presenting experimental data.

[b]ND, not determined.

[c]Yttria concentrations for various yttria-stabilized zirconias used are specified in tables presenting experimental data.

TABLE II - THE EFFECT OF YTTRIUM CONCENTRATION IN THE BOND COATING AND YTTRIA CONCENTRATION IN THE THERMAL BARRIER COATING ON THE PERFORMANCE OF A TWO-LAYERED THERMAL BARRIER SYSTEM AS DETERMINED BY CYCLIC FURNACE TESTING BETWEEN 990° and 280° C[a]

Bond coating		Thermal barrier coating		Cycles to failure[b]
Composition, wt %	Thickness, cm	Composition, wt %	Thickness, cm	
Ni-16.4Cr-5.1Al-0.15Y	0.011	ZrO_2- 4.0Y_2O_3	0.039	1206
Ni-17.0Cr-5.4Al-0.35Y	.011	- 4.0Y_2O_3	.038	1482
Ni-16.3Cr-4.9Al-0.61Y	.010	- 4.0Y_2O_3	.037	1130
Ni-16.6Cr-5.5Al-1.08Y	.012	- 4.0Y_2O_3	.036	846
Ni-16.4Cr-5.1Al-0.15Y	0.011	ZrO_2- 6.2Y_2O_3	0.039	[c]1500
Ni-17.0Cr-5.4Al-0.35Y	.010	- 6.2Y_2O_3	.038	[c]1500
Ni-16.3Cr-4.9Al-0.61Y	.011	- 6.2Y_2O_3	.038	[c]1500
Ni-16.6Cr-5.5Al-1.08Y	.013	- 6.2Y_2O_3	.040	[c]1500
Ni-16.4Cr-5.1Al-0.15Y	0.012	ZrO_2- 7.9Y_2O_3	0.038	[c]1498
Ni-17.0Cr-5.4Al-0.35Y	.010	- 7.9Y_2O_3	.037	[c]1210
Ni-16.3Cr-4.9Al-0.61Y	.009	- 7.9Y_2O_3	.038	738
Ni-16.6Cr-5.5Al-1.08Y	.010	- 7.9Y_2O_3	.038	715
Ni-16.4Cr-5.1Al-0.15Y	0.013	ZrO_2-11.5Y_2O_3	0.039	1440
Ni-17.0Cr-5.4Al-0.35Y	.011	-11.5Y_2O_3	.043	813
Ni-16.3Cr-4.9Al-0.61Y	.012	-11.5Y_2O_3	.036	665
Ni-16.6Cr-5.5Al-1.08Y	.010	-11.5Y_2O_3	.050	526
Ni-16.4Cr-5.1Al-0.15Y	0.010	ZrO_2-17.4Y_2O_3	0.040	535
Ni-17.0Cr-5.4Al-0.35Y	.009	-17.4Y_2O_3	.040	319
Ni-16.3Cr-4.9Al-0.61Y	.009	-17.4Y_2O_3	.041	246
Ni-16.6Cr-5.5Al-1.08Y	.009	-17.4Y_2O_3	.036	233
Ni-17.0Cr-5.4Al-0.035Y	0.012	ZrO_2-24.4Y_2O_3	0.029	248
Ni-16.3Cr-4.9Al-0.61Y	.009	-24.4Y_2O_3	.037	179
Ni-16.6Cr-5.5Al-1.08Y	.009	-24.4Y_2O_3	.036	147

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[a] B-1900 alloy with 2 weight percent Hf was used as a substrate material; specimens were about 2.5x1.3x0.25 cm. A minimum of two specimens were run per each test.

[b] Cycle consisted of 6 minutes heat up, 60 minutes at temperature, 60 minutes cooling to about 280° C. Test stopped whenever a crack occurred. Specimens inspected every 12 cycles.

[c] No failure.

TABLE III - THE EFFECT OF YTTRIUM CONCENTRATION IN THE BOND COATING AND YTTRIA CONCENTRATION IN THE THERMAL BARRIER COATING ON THE PERFORMANCE OF TWO-LAYERED THERMAL BARRIER SYSTEM AS DETERMINED BY CYCLIC FURNACE TESTING BETWEEN 1095° and 280° C[a]

Bond coating		Thermal barrier coating		
Composition, wt %	Thickness, cm	Composition, wt %	Thickness, cm	Cycles to failure[b]
Ni-16.4Cr-5.1Al-0.15Y	0.010	ZrO_2- 4.0Y_2O_3	0.042	80
Ni-17.0Cr-5.4Al-0.35Y	.010	- 4.0Y_2O_3	.038	82
Ni-16.3Cr-4.9Al-0.61Y	.009	- 4.0Y_2O_3	.037	52
Ni-16.6Cr-5.5Al-1.08Y	.010	- 4.0Y_2O_3	.041	41
Ni-16.4Cr-5.1Al-0.15Y	0.010	ZrO_2- 6.2Y_2O_3	0.040	112
Ni-17.0Cr-5.4Al-0.35Y	.011	- 6.2Y_2O_3	.038	88
Ni-16.3Cr-4.9Al-0.61Y	.010	- 6.2Y_2O_3	.038	70
Ni-16.6Cr-5.5Al-1.08Y	.010	- 6.2Y_2O_3	.043	58
Ni-16.4Cr-5.1Al-0.15Y	0.012	ZrO_2- 7.9Y_2O_3	0.042	102
Ni-17.0Cr-5.4Al-0.35Y	.014	- 7.9Y_2O_3	.044	82
Ni-16.3Cr-4.9Al-0.61Y	.012	- 7.9Y_2O_3	.044	72
Ni-16.6Cr-5.5Al-1.08Y	.011	- 7.9Y_2O_3	.039	66
Ni-16.4Cr-5.1Al-0.15Y	0.011	ZrO_2-11.5Y_2O_3	0.044	74
Ni-17.0Cr-5.4Al-0.35Y	.013	-11.5Y_2O_3	.039	67
Ni-16.3Cr-4.9Al-0.61Y	.012	-11.5Y_2O_3	.039	64
Ni-16.6Cr-5.5Al-1.08Y	.012	-11.5Y_2O_3	.043	38
Ni-16.4Cr-5.1Al-0.15Y	0.013	ZrO_2-17.4Y_2O_3	0.038	42
Ni-17.0Cr-5.4Al-0.35Y	.012	-17.4Y_2O_3	.030	44
Ni-16.3Cr-4.9Al-0.61Y	.014	-17.4Y_2O_3	.046	20
Ni-16.6Cr-5.5Al-1.08Y	.011	-17.4Y_2O_3	.036	18
Ni-17.0Cr-5.4Al-0.35Y	0.010	ZrO_2-24.4Y_2O_3	0.040	23
Ni-16.3Cr-4.9Al-0.61Y	.011	-24.4Y_2O_3	.039	18
Ni-16.6Cr-5.5Al-1.08Y	.012	-24.4Y_2O_3	.035	18

[a] B-1900 alloy with about 2 weight percent Hf was used as a substrate material; specimens were about 2.5x1.3x0.25 cm. A minimum of two specimens were run per each test.

[b] Cycle consisted of 6 minutes heat up, 60 minutes at temperature, 60 minutes cooling to about 280° C. Test stopped whenever a crack occurred. Specimens inspected at least once every 12 cycles.

TABLE IV - THE RELATIONSHIP BETWEEN THE PHASES PRESENT IN THE THERMAL BARRIER COATING AND THE PERFORMANCE OF THE TWO-LAYERED THERMAL BARRIER SYSTEM CONSISTING OF Ni-17.0w/oCr-5.4w/oAl-0.35w/oY BOND COATING AND YTTRIA-STABILIZED ZIRCONIA AS DETERMINED BY CYCLIC FURNACE TESTING BETWEEN 990° and 270° C[a]

Thermal barrier coating composition, wt %	Phases present before testing			Phases present after testing			Cycles to failure[b]
	Cubic	Monoclinic	Y_2O_3	Cubic	Monoclinic	Y_2O_3	
$ZrO_2-4.0Y_2O_3$	Major	Major	None	Major	Major	None	1482
$ZrO_2-6.2Y_2O_3$	Major	Major-minor	None	Major	Minor	None	[d]1500
$ZrO_2-7.9Y_2O_3$	Major	Minor	None	Major	V Minor	None	[d]1210
$ZrO_2-11.5Y_2O_3$	Major	V Minor[c]	V Minor	Major	VV Minor	None	830
$ZrO_2-17.4Y_2O_3$	Major	VV Minor	Minor	Major	None	Minor	319
$ZrO_2-24.4Y_2O_3$	Major	VV Minor	Minor	Major	None	Minor	248

[a] B-1900 alloy with Hf was used as a substrate material; specimens were about 2.5x1.3x0.25 cm. A minimum of two specimens were run per each test. At least two samples per each composition were analyzed by X-ray diffraction.

[b] Cycle consisted of 6 minute heat up, 60 minutes at temperature, 60 minutes cooling to about 270° C. Test stopped whenever a crack occurred.

[c] V = very; VV = very, very.

[d] No failure.

TABLE V - THE EFFECTS OF [illegible]IUM CONCENTRATION IN THE BOND COATING AND YTTRIA CONCENTRATION IN THE STANDARD PURITY THERMAL BARRIER COATING ON THE PERFORMANCE OF THE TWO-LAYERED THERMAL BARRIER SYSTEM AS DETERMINED BY CYCLIC TESTING IN NATURAL GAS-OXYGEN TWO-TORCH BURNER RIG[a]

Bond coating		Thermal barrier coating		Cyclic temp., °C	Cycles to failure[b]
Composition, wt %	Thickness, cm	Composition, wt %	Thickness, cm		
Ni-16.4Cr-5.1Al-0.15Y	0.013	ZrO_2- 4.0Y_2O_3	0.040	1205	466
Ni-17.0Cr-5.4Al-0.35Y	.010	- 4.0Y_2O_3	.036	1195	494
Ni-16.4Cr-5.1Al-0.15Y	0.011	ZrO_2- 6.2Y_2O_3	0.037	1205	792
Ni-17.0Cr-5.4Al-0.35Y	.008	- 6.2Y_2O_3	.036	1200	629
Ni-16.4Cr-5.1Al-0.15Y	0.013	ZrO_2- 7.9Y_2O_3	0.037	1190	588
Ni-17.0Cr-5.4Al-0.35Y	.010	- 7.9Y_2O_3	.032	1200	407
Ni-16.3Cr-4.9Al-0.61Y	.009	- 7.9Y_2O_3	.031	1195	56
Ni-16.6Cr-5.5Al-1.08Y	.008	- 7.9Y_2O_3	.032	1195	50
Ni-16.4Cr-5.1Al-0.15Y	0.011	ZrO_2-11.5Y_2O_3	0.032	1190	186
Ni-17.0Cr-5.4Al-0.35Y	.008	-11.5Y_2O_3	.042	1200	157
Ni-16.3Cr-4.9Al-0.61Y	.009	-11.5Y_2O_3	.035	1195	38
Ni-16.6Cr-5.5Al-1.08Y	.009	-11.5Y_2O_3	.037	1200	42
Ni-17.0Cr-5.4Al-0.35Y	0.010	ZrO_2-17.4Y_2O_3	0.032	1200	75
Ni-16.3Cr-4.9Al-0.61Y	.010	-17.4Y_2O_3	.044	1185	48
Ni-16.6Cr-5.5Al-1.08Y	.012	-17.4Y_2O_3	.030	1190	40
Ni-17.0Cr-5.4Al-0.35Y	0.012	ZrO_2-24.4Y_2O_3	0.034	1190	36
Ni-16.3Cr-4.9Al-0.61Y	.009	-24.4Y_2O_3	.030	1200	27
Ni-16.6Cr-5.5Al-1.08Y	.012	-24.4Y_2O_3	.030	1185	32

[a] MAR-M-509 alloy was used as a substrate material. Specimens were about 7.5x1.3x0.5 cm. A minimum of two specimens were run per each test.

[b] Cycle consisted of 3 minutes heat up, 60 minutes at temperature, and 5 minutes cooling to about 100° C. Testing stopped whenever a crack occurred. Specimens inspected almost every 4 cycles.

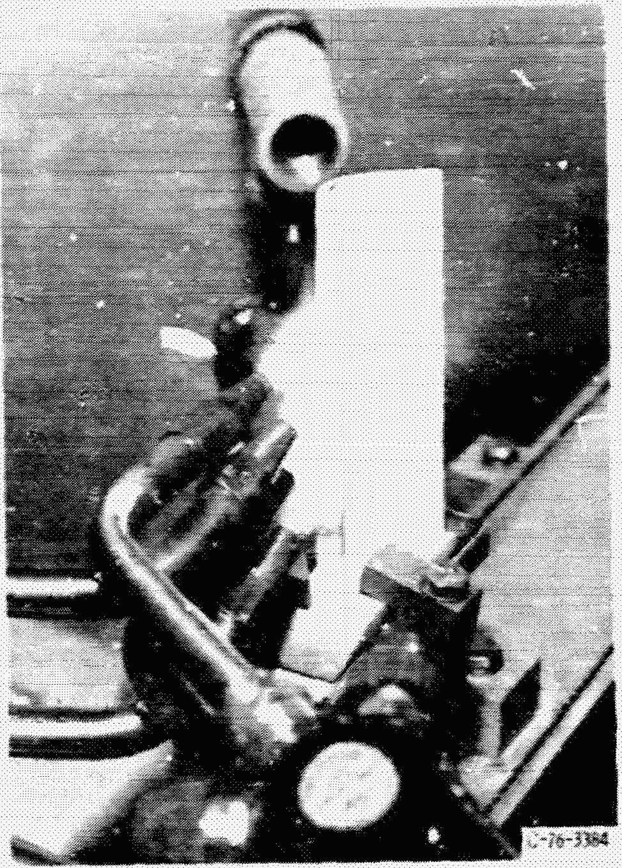


Figure 1. - Natural gas-oxygen torch burner rig and J-75 blade coated with NiCrAlY bond coating and ZrO_2-Y_2O_3 thermal barrier coating.

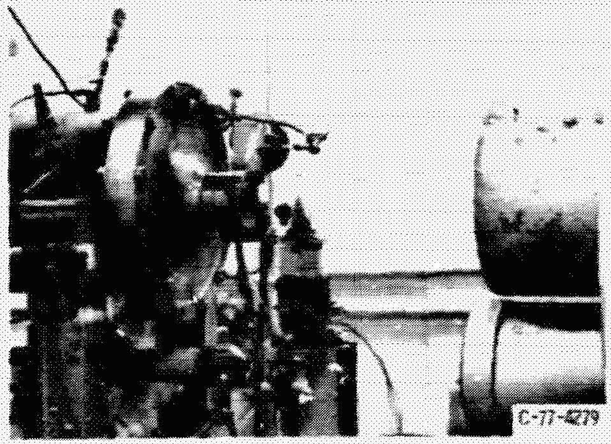
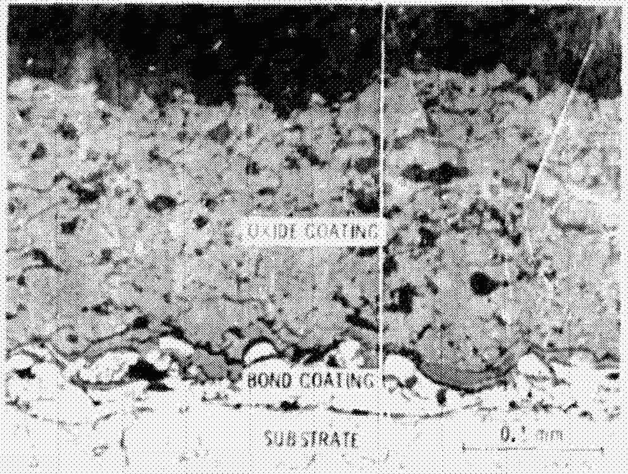
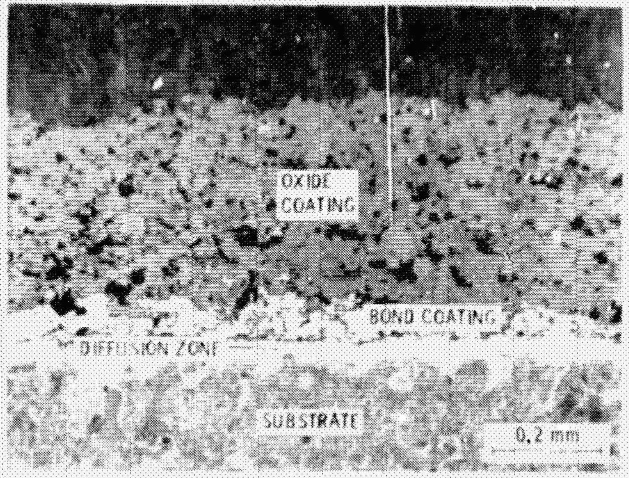


Figure 2. - Mach 0.3 combustion burner rig and J-75 blade coated with NiCrAlY bond coating and ZrO_2-Y_2O_3 thermal barrier coating.



(a) BEFORE TESTING.



(b) AFTER TESTING FOR 1498 CYCLES AT 990° C. (CYCLE, 6 MINUTES HEAT UP, 60 MINUTES AT TEMPERATURE, AND 60 MINUTES COOLING TO ABOUT 280° C).

Figure 3. - Light optical photomicrograph of B-1900 with Hf coupon specimen coated with Ni-16.4Cr-5.1Al-0.15Y bond coating and ZrO_2-7.9Y_2O_3 thermal barrier coating.

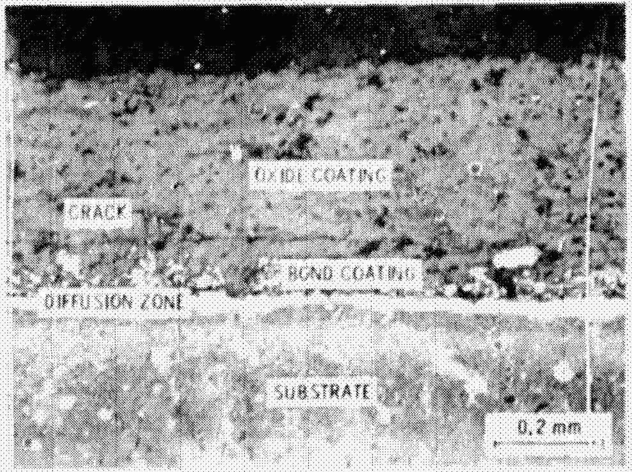


Figure 4. - Light optical photomicrograph of MAR-M-509 coupon specimen coated with Ni-16.4Cr-5.1Al-0.35Y and ZrO_2-7.9Y_2O_3 after testing for 1520 cycles at 990° C. (Cycle, 6 minutes heat up, 60 minutes at temperature, 60 minutes cooling to about 280° C).

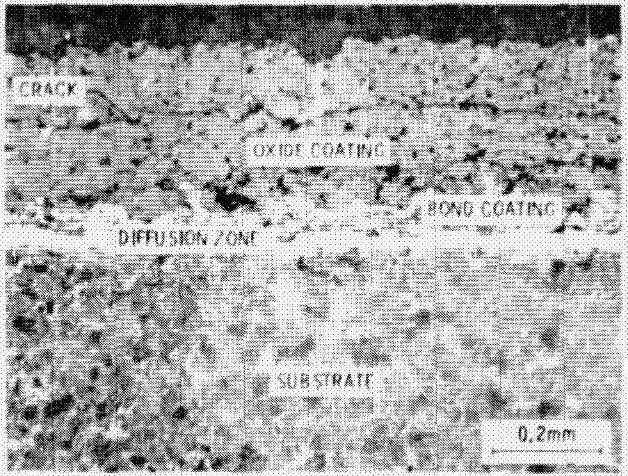


Figure 5. - Light optical photomicrograph of MAR-M-509 coupon specimen coated with Ni-17.0Cr-5.4Al-0.35Y and ZrO_2-7.9Y_2O_3 after testing in cyclic natural gas-oxygen burner rig for 400 cycles at 1200° C. (Cycle, 3 minutes heat up, 60 minutes at temperature, and 5 minutes cooling to about 100° C).

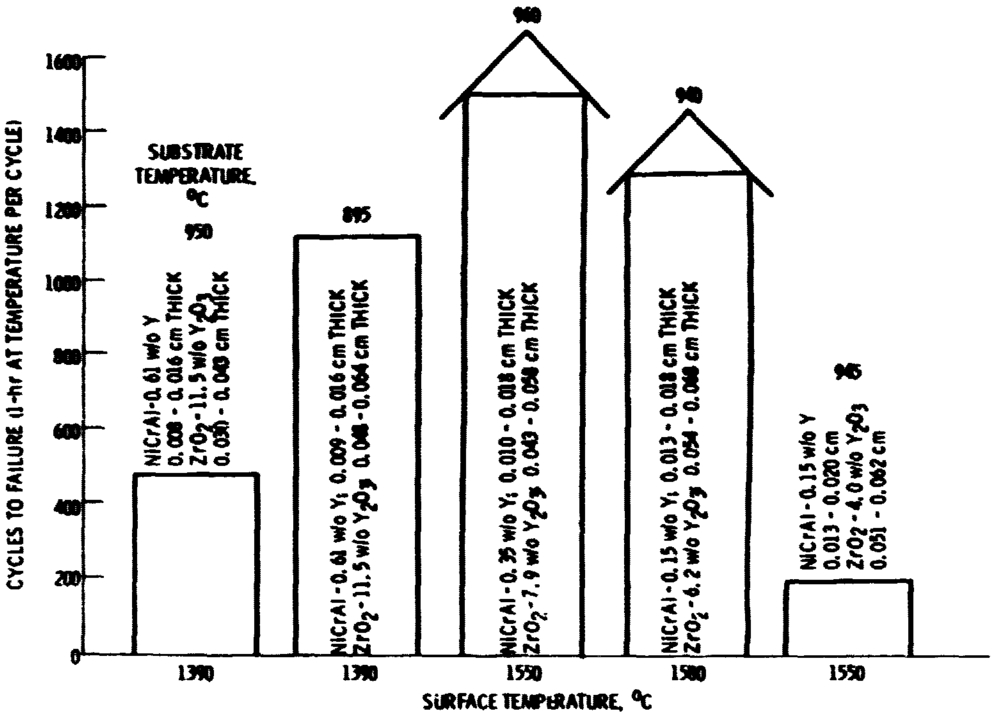
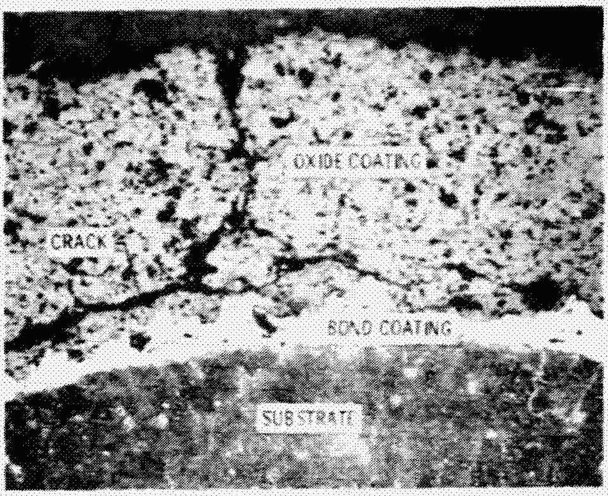
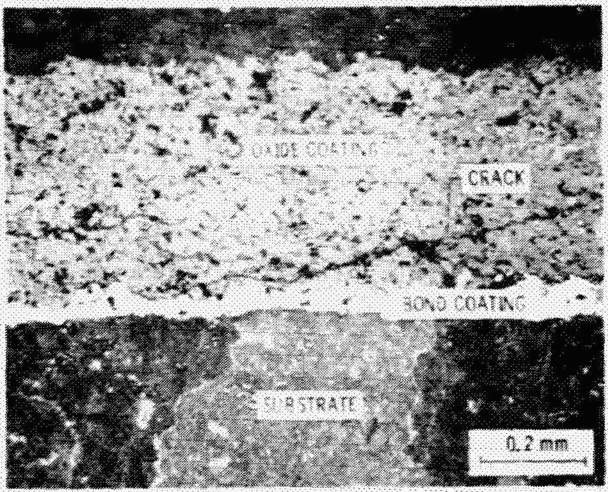


Figure 6. - Performance of thermal barrier coating systems on air-cooled blades in cyclic natural gas-oxygen torch burner rig.



(a) PERPENDICULAR CRACK.



(b) ACUTE ANGLE CRACK.

Figure 7. - Light optical photomicrograph of B-1900 J-75 blade coated with Ni-16.3Cr-4.9Al-0.61Y bond coating and ZrO_2-11.5Y_2O_3 thermal barrier coating after testing for 1120 1-hour cycles at 1390° C surface temperature.

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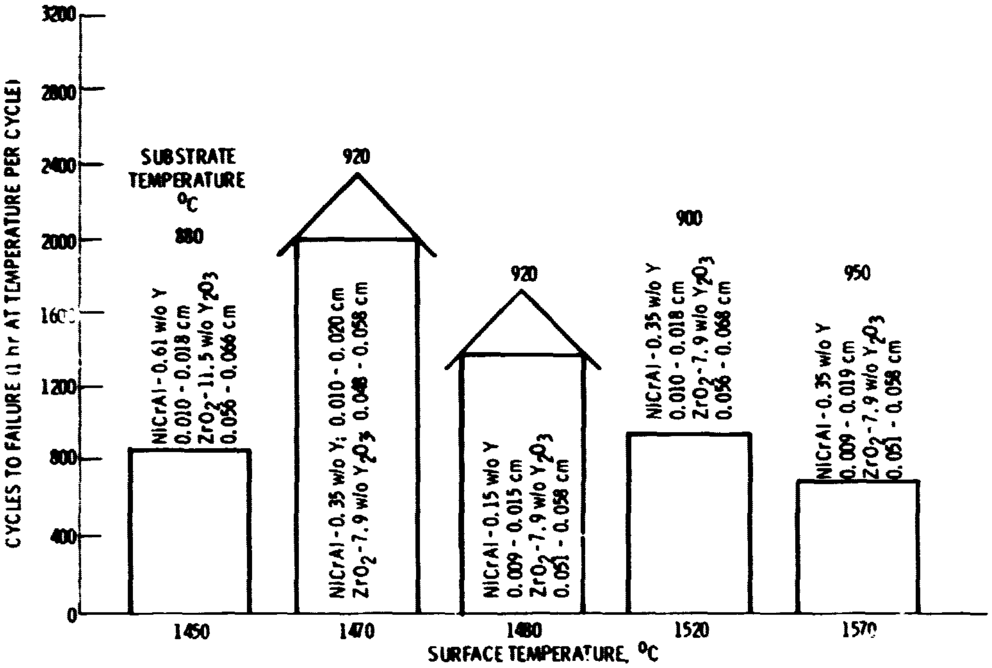

Figure 8. - Performance of various thermal barrier coating systems in cyclic Mach 1.0 burner rig.